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Research Reactor FR 2

**20 Years Chemical and
Radiochemical Measurements**

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RESEARCH REACTOR FR2 : 20 YEARS CHEMICAL AND RADIOCHEMICAL
MEASUREMENTS *

Abstract

The FR2 has been a D₂O cooled and moderated research reactor with a thermal output of 44 MW. It was in operation from 1961 to 1981.

Because of the operating conditions of the reactor, only a small number of routine measurements were performed. For these however special techniques had to be developed. During the 20 years of operation a number of special events occurred or have been observed, sometimes with very amazing results, e.g. the 'acetone effect'.

This report describes the chemical and radiochemical conditions of the reactor systems, as well as the results of the surveillance work. Not described are measurements for the many experiments. The last chapter gives in a short form a description of the most unusual events and observations.

FORSCHUNGSREAKTOR FR2 : 20 JAHRE CHEMISCHE UND RADIOCHEMISCHE
UNTERSUCHUNGEN *

Zusammenfassung

Der Reaktor FR2 war ein Schwerwasser-moderierter und -gekühlter Forschungsreaktor mit einer thermischen Leistung von 44 MW. Er wurde von 1961 bis 1981 betrieben.

Durch die günstigen Betriebsbedingungen waren nur eine geringe Anzahl an Routinemessungen erforderlich. Für diese mußten jedoch spezielle Methoden entwickelt werden. Während der 20 Betriebsjahre traten eine Reihe spezieller Ereignisse ein, die manchmal erstaunliche Effekte zeigten; z.B. der von uns so genannte 'Aceton-Effekt'.

Der Bericht beschreibt die chemischen und radiochemischen Zustände der Reaktorsysteme und die Ergebnisse der Überwachungsanalytik. Nicht beschrieben werden Arbeiten für die zahlreichen Reaktorexperimente. Im letzten Abschnitt werden einige besondere Vorkommnisse und Beobachtungen beschrieben.

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Abstract

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1. Introduction

The reactor FR2 was the first german build reactor. FR2 is standing for Forschungsreaktor number 2. After a designing and construction time of approximately 6 years, full power with the first core was reached in december 1962. Until its final shutdown in december 1981, the reactor was used very effectively for many kinds of experiments.

The 20 years FR2 were actually 20 years of nuclear research from the beginning. We had to learn nearly everything around a reactor. Many chemical standard techniques could not be used because of the radioactivity, or because unusual low detection limits were required for some elements in different materials. The stability of many materials, especially plastics against radiation was not known. In addition, in pile experiments with high temperature steam, high pressure water or helium, as well as with liquid hydrogen or helium at temperatures just a few degrees above the absolute zero raised many more unusual chemical questions.

This paper will describe in a short form the work of the chemistry group at the FR2. It will concentrate mainly on measurements, required for the operation of the reactor. Discussing also measurements for experiments would make the paper endless. In the last chapter some special events during the life of the reactor will be listed, events naturally interesting for chemists.

2. The reactor FR2

The reactor FR2 has been a heavy water cooled and moderated research reactor. The operation temperature was well below the boiling point of the water, therefore the primary system could operate without any overpressure. The covergas was helium. The secondary system was operated with demineralized water. The heat was dispatched to the atmosphere by open cooling towers. Furthermore a number of auxillary systems required some chemical control.

From 1962 until 1966 the reactor had a thermal output of 12 MW. During this time, metallic fuel elements with natural uranium, stabilized by 1% niobium, were used, the cladding was aluminum. The maximum thermal neutron flux was $3 \cdot 10^{13}$ [n/cm²•s] . The maximum temperature of the heavy water at the core outlet was 50 °C.

With the modification of the core in the summer 1966 , the thermal output was raised to 44 MW, the maximum thermal neutron flux to $1 \cdot 10^{14}$ [n/cm²•s] . In this core low enriched oxide fuel was used, the cladding material was zircaloy. The core outlet temperature was now around 85 °C.

The reactor was operated under this conditions until its final shutdown.

In the following description only these reactor systems will be mentioned, which were of some interest for chemical surveillance or studies. The descriptions will be as short as possible, more details can be seen in (1).

2.1 The primary system

The primary system was the most important part of the FR2 for the chemical surveillance. Because of the neutron activation it was kept under extremely clean conditions. The heavy water was very rare and expensive at this time, therefore the control of the concentration of D_2O was a major objective during the first years.

Figure 1 shows a schematic flow diagram of the primary system, table 1 some data.

The main coolant flow was $2000 \text{ m}^3/\text{h}$. The purification system consisted of 180 liters of a 1 to 1 mixture of anionic and cationic resins (table 1), it was operated with a bypass flow of $2.5 \text{ m}^3/\text{h}$. The resins were used in the H^+ resp. OH^- form.

Actually the primary loop contained 5 pumps and heat exchangers, the purification system two lines in parallel. Not shown are emergency and auxiliary systems, systems for the automatical control of cladding failures or the measurements of the pD -values and the electrical conductivity of the heavy water.

Important for some discussions below is the fact, that the overflow of the core, $8 \text{ m}^3/\text{h}$, were flowing through a covergas phase into the 5 m^3 tank. The degassing of this water was nearly complete.

2.2 The covergas system

Figure 2 shows a schematic flow diagram of the covergas system.

The covergas of the FR2 was helium. This gas was used because of its low neutron cross section for activation, and its good heat conductivity. An disadvantage was the high price.

About 20 m³ of helium were flowing, passing over all surfaces of the heavy water. The helium pressure was maintained to 10 mbar.

The helium collected the gases formed by the radiolytic decomposition of the D₂O. The formed deuterium was reconverted to D₂O by a CuO - catalyst in a recombiner furnace. The covergas also collected fission gases and other radioactive gaseous nuclides.

During operations at the reactor, always some air was introduced. With air concentration in the range of a few percent by volume, a purification system was started, removing the impurities with a liquid nitrogen cooled charcoal trap. This trap was later heated up and the impurities released to the stack.

Automatic analytical instrumentation controlled the deuterium concentration, as well as oxygen and nitrogen.

2.3 The secondary system

The produced heat was transferred in five heat exchangers from the D₂O to the secondary system. Here about 500 m³ demineralized water circulated over open cooling towers. On hot dry weather conditions, about 1 ton of water evaporated per MWh. This had to be replaced by fresh demineralized water.

The demineralizer facility was automatically controlled and caused very seldom problems. However when the fresh water quality changed from 1967 to 1970, it had to be upgraded.

Because of the open cooling towers a make-up demineralizer was required. The total system was installed by such way, that the make-up system removed also the SiO₂ while the CO₂ was removed by degassing in the cooling towers.

2.4 Other systems

There were a number of other parts or systems of the reactor, occasionally of interest for the chemists. From this two will be mentioned here.

While the primary vessel was made from aluminum , the first biological shield was a double walled steel tank. Between the walls was a cast lead shield, cooled by demineralized water in stainless steel coils.

Most of the experimental channels and other openings were cooled by air. This air was released together with the building exhaust to the atmosphere through a 100 m high stack. A maximum of 100,000 m³/h of air passed the stack.

3. Measurements at the FR2

Table 2 summarizes the working fields of the chemistry group. Some of the measurements had to be done daily or weekly, the largest number however upon request from the reactor operators or some experimentalists.

3.1 Primary system

3.1.1 Isotopic concentration of the heavy water

To maintain the isotopic concentration of the primary coolant as high as possible has been a major concern of the operators during all the 20 years of operation. Therefore also the determination of this concentration has been one of the most important objectives for the chemistry. A total of about 6000 samples were analyzed, an average of one sample per day.

Until 1967 the isotopic concentration was evaluated from the density of the water(2). The floating temperature of a calibrated float was determined to better than ± 0.005 °C. The water had to be purified by distillation and carefully degassed. The overall accuracy in the most interesting concentration range above 99.6 mol% was ± 0.003 mol*

The float-method was very time consuming. Furthermore when searching for sources of small amounts of H₂O, leaking into the heavy water, the accuracy has not been sufficient. A new method was developed and used until the final shutdown . The new method used the already available spectral photometer PMQ-II (Zeiss); by measuring in the near IR range the accuracy

could be improved to ± 0.0015 mol% (3).

(The new method actually measured the HDO- concentration in the sample. The relative accuracy, related to the HDO concentration, was 0.2 to 0.4%)

Figure 3 shows the development of the isotopic concentration during the 20 years FR2. In 1966 and in 1976 new heavy water with a higher concentration was added to the system. Except for the first few years the average decrease per year was 0.012 mol%, equivalent of adding about 3 kg of H₂O to the coolant.

This ordinary water came from many sources.

Exchange of fuel elements or experimental facilities introduced water because of humidity on surfaces, air leaks to the covergas added also humidity, and some water was released from the deuterated ion exchange resins . The resins were deuterated before the use by replacing the H₂O by D₂O (4). The heavy water flowed upwards with a speed of 0.07 cm/min. The deuteration was stopped when the water at the outlet had a concentration very near to the inlet concentration. Nevertheless about 300 g of H₂O get released during one year of operation from 180 l of resin (5).

3.1.2 Purity of the heavy water

As mentioned before, the primary coolant was kept as clean as possible. Because of the very effective purification system the electrical conductivity was well below 1 μ S/cm, the pD value at 6.8 . The corrosion rate of the structural materials was therefore very low.

Table 3 shows the concentrations of the most important impurities. The analysis was done during the first years

monthly, later on only occasionally. For the determination of the metallic elements samples of 2 kg heavy water were used, photometric methods were applied.

Uranium was determined by a fluorometric method. 50 g samples of heavy water were evaporated, adding deuterated nitric acid to avoid adsorption losses. The residue was mixed with NaF and molten. The formed glass was measured. $2 \cdot 10^{-8}$ grams U per sample could be detected, corresponding to $4 \cdot 10^{-4}$ ppm. Usually no uranium was detected. Sometimes however nonvisible particles were in the sample, containing up to 1 μ g of U. These particles were introduced into the system during the large cladding defect of a metallic fuel element in 1963 (s. below).

Chlorine and sodium were determined by neutron activation analysis.

The concentration of particulate material was not reproducible. The value was always below 10 ppm. Particulate material was found as crud on the ion exchangers.

3.1.3 Corrosion of structural material

From the data given in 3.1.2 and the flow rate over the purification system of 2.5 m³/h, total corrosion rates can be estimated. Of course only dissolving corrosion values are obtained, no statements can be made about surface layers.

The found corrosion rates were :

Al-99.5	0.06 mdd	=	0.8 μ /y
Steel	0.04 mdd	=	0.2 μ /y.

These values are a factor of 4 (for aluminum) respectively 2 (for stainless steel) higher than values evaluated and measured in 1959 by Mittenbühler (7) for 50 °C. Considering the very different conditions in small scale experiments and the real reactor system, the agreement is very good.

3.1.4 Alpha activity (Table 4)

Alpha activity was not measured before the large cladding defect in 1963. Later on the activity was measured in samples of 50 grams of heavy water. An electroplating technique was used for the preparation (6). For spectroscopic measurements larger samples were used.

The alpha activity was found in the range of 4 to 20 $\cdot 10^{-5}$ Bc/g coolant (1 to 5 $\cdot 10^{-3}$ pCi/g). Always Pu-239 caused more than 50% of the activity, the remaining coming from other transuranium elements. Only a minor fraction came from uranium, as could be expected from the values given before.

Sometimes cladding defects caused higher values of alpha activity in the coolant. Alpha spectroscopy showed in two cases, that the defect elements were special Pu-irradiation capsules.

One example is given here:

On January 8, 1979, $5 \cdot 10^{-3}$ Bc/g were found.

This activity consisted of

54	%	Pu-239
3	%	Pu-238/Am-241
8	%	Pu-242
1.5	%	Cf-252
31	%	U-238
		(rem. unidentified)

From the irradiation history and these values the capsule could be identified.

3.1.5 Beta activity (Table 4)

Only two beta-emitting nuclides were of interest at the FR2 : tritium and C-14.

Tritium was an 'intrinsic' nuclide of the coolant, formed by the (n, γ) reaction from the deuterium. Its value increased in agreement with the radioactive build-up and decay functions steadily, and was reduced twice because of adding fresh coolant (s. 3.1.1). Its final value was $2.4 \cdot 10^8$ Bc/g (6.5 mCi/g). Tritium was the nuclide with the highest activity in the primary coolant.

C-14 was formed by 3 different reactions. Dominant were the reactions

O-17 (n, α) C-14

N-14 (n,p) C-14

while the direct activation of carbon impurities played only a minor role.

Because C-14 was dissolved in the water completely

as CO₂, it was removed together with all other impurities by the purification system. On the other hand, the ion exchange resins were highly loaded with CO₂ (below), therefore the water contained always an equilibrium concentration.

It is therefore not possible to evaluate the production of C-14 from the analysis of the coolant and the purification rate. From the investigation of the resins it was calculated, that per year about $1.2 \cdot 10^{11}$ Bq (3.3 Ci) of C-14 has been formed.

It has been remarkable that the specific activity of carbon has been nearly constant over all the time. The value was

$$2 \pm 0.5 \cdot 10^8 \text{ Bq/g carbon}$$

This is probably the equilibrium value between production and removing by the purification system. Only a small fraction was found in the covergas.

(During the first years with a thermal output of only 12 MW, the specific activity was a factor of three lower, in agreement with the 3 times lower neutron flux)

3.1.6 Gamma activity (Table 4)

Until we could buy our first Ge(Li) detector in 1971, many radiochemical separation were required to identify nuclides. With the high resolution gamma spectroscopy more than 100 radioactive nuclides were found. All fission product isotopes were included, besides corrosion product elements and activation products of the coolant and of impurities.

Table 4 contains only the most important nuclides for the

reactor operation.

N-16, O-19, F-17 and F-18 are the intrinsic nuclides of the heavy water. They are formed by the reactions

O-16 (n,p) N-16

O-18 (n, γ) O-19

O-16 (d,n) F-18

O-16 (d,2n) F-17.

The first two nuclides were expected from the beginning. N-16 required in some areas of the reactor special shieldings because of its highly penetrating gamma rays (up to 7 MeV). Surprising for us have been the two fluorine isotopes. The 511 keV annihilation radiation has been the strongest peak in the spectra after a few minutes decay time. Fast neutrons transfer sufficient energy to deuterium-nucleus to form deuterons for the reactions.

The fission and corrosion product nuclides need no detailed discussion. Fission product values as given in the table were obtained without defective fuel elements, they are formed from tramp fuel fissions. Cs-138 was measured also on-line by high resolution gamma spectroscopy for the detection of fuel failures. (Measurement of the water in a chamber after passing an anionic ion exchanger for removing the fluorines).

The source of the Tc-99m and Re-188 was found to be MoS₂, frequently used at the FR2 as a lubricant. Surprisingly was the activity of the precursor Mo-99 extremely low, at least a factor of 1000 lower than expected. Obviously the molybdenum gets plated out on surfaces and the decay product Tc-99m is released by recoil. This effect however can not be explained satisfactory, because Tc as well as Re are rather noble metals and should plate out as well. Also the rhenium concentration in the lubricant has been very small, its activity however much larger than these of Tc-99m. That means, a fraction of the technetium remains also deposited. From the electrochemical

potential one would expect an opposite behavior, because the Re is more noble than the Tc. On the other hand, the oxygen potential of the heavy water, caused by the D_2O_2 (below) is not high enough to form compounds of these elements with higher valency.

Ag-110m was found always in the water since 1966. For some time it caused a serious contamination problem. This will be described in the last chapter of this paper.

3.1.7 Surface contamination and tramp fuel

All parts and components, removed from the primary system, were contaminated. After washing off the heavy water and with this the tritium, alpha and gamma contamination had to be considered.

Table 5 shows the equilibrium values of the surface contamination during the last years of reactor operation. Listed are values for smooth surfaces. In flow disturbed areas as valves etc., up to a factor of 10 higher values were found.

The alpha contamination was of special interest, because it included the contamination by fuel, and was the source for the tramp fuel fissions. These in turn were responsible for the fission product levels in the primary system without defective fuel elements.

As in the case with the alpha activity in the coolant (above), more than 50% was caused by contamination with Pu-239. The total amount of plutonium on the surfaces of the primary system of course was very low (0.02 to 0.2 mg).

The contamination with uranium was constant since 1966. It was determined by two ways : Washing from surfaces with

acids and fluorometric determination as described before, and also from the total number of tramp fuel fissions. The latter was derived from the measurement of fission products and an average neutron flux in the core of $1 \cdot 10^{13}$ [n/cm²·s]. The uranium contamination was the same on stainless steel, aluminum and zircaloy. The value was around 1 mg/m², corresponding to a total amount of uranium on all surfaces of the primary system of about 1 g.

The number of tramp fuel fissions was found to $5 \cdot 10^{10}$ f/s. Because the uranium concentration in the zircaloy cladding was below 1 ppm, the contamination with uranium was responsible for the tramp fuel fissions.

The reactor is now in the decommissioning phase. It was found, that even after strong decontamination and removal of the surfaces of steel some activity remained. The activity concentration was a function of the distance from the core. After 20 meter of piping about 1 Bq/g steel was found for Co-60. This Co-60 was formed by activation with neutrons, produced by the reactions

O-17 (n,p) N-17

N-17 (,βn) O-16

The activation followed along the piping the decay of the N-17 (half live 4.2 s). The 20 m piping were a transport time for the heavy water of 2.5 seconds. The calculated neutron flux at this position was 10^3 [n/cm²·s] (8).

3.1.8 Radiolytic decomposition of the heavy water,
Isotopic effects

By measuring the production rate of deuterium it was found, that per MWh 0.22 grams of D_2O were decomposed by radiolysis. With the full power of 44 MW, 260 liters of D_2 were formed per day.

The dose rate in the core during full power operation was measured to 200 MRad/h. With this a G -value for the deuterium productions was calculated to

$$G \sim 10^{-3}$$

(G = formed atoms per 100 ev absorbed energy).

The concentration of the formed D_2O_2 was not constant. It was in the range of 1 to 10 ppm, corresponding to 30 to 300 grams of peroxyde in the coolant.

For the lay-out of the primary system of the reactor it was assumed, that 0.15 grams of D_2O will decompose per MWh. The result of the measurements is in a good agreement with this assumed value.

(From the japanese reactor JRR-3 a value of 0.17 g D_2O decomposition per MWh is reported, while at the reactor JRR-2 12 g decompose(9). The latter reactor had very high impurity levels in the primary coolant; the corrosion rate has been so high, that a milky suspension of aluminum hydroxid was circulating.)

The only isotopic separation effect seen at the reactor FR2 was for the radiolytic decomposition of the heavy water. The D_2O concentration from the reconverted deuterium was

always in the range of 99.5 mol%, while the bulk heavy water had a concentration at 99.7 mol% .

3.1.9 Studies at the purification system

The purification system had for all nuclides with the exception of the rare gases decontamination factors between 100 and 1000. Break-through was detected, when the electrical conductivity at the outlet raised. Usually the exchanger resins could be used for one year or longer. The resins got de-deuterated (method as described before) and stored as radioactive waste.

Loaded resins were studied in 1964 and 1972. The resins were heavily loaded with black crud, which could not be removed completely by floating techniques. The anionic resin M500 was saturated with CO₂, while the cationic resin S100 still had about 30% of its capacity. The loaded M500 contained about 2 to 3 kg of CO₂ with 3.3 Ci of C-14. The anionic resin was therefore always responsible for the break through. For different reasons however the ratio of the mixture was not changed.

3.2 Covergas system

The fission gases were routinely measured twice a week by gamma spectroscopy. The in-line instrumentation was occasionally recalibrated and controlled by laboratory measurements.

In order to learn more about delay times when detecting cladding defects by fission gases in the covergas, the average degassing delay has been determined. Fig.4 shows

relative release to birth ratios as a function of the decay constants of the fission gases. While the degassing of the bulk heavy water is delayed by about one day, the degassing in the overflow tank (5 m³ tank, fig.1) is nearly instantaneous.

From the values of dissolved gases (in D₂O) and the concentration in the covergas, Henry-constants were derived. Only for the covergas helium the found value was in agreement with estimations from the literatur. Other equilibria are disturbed. E.g. deuterium is removed from the gas by the recombiner, oxygen undergoes chemical reactions, radioactive gases decay. In all these cases the equilibrium between the liquid and the gas phase is shifting. The Xe-133 distribution coefficient (half live 5.3 days) approached nearly the theoretical value, if the covergas system had operated for a long time without purification.

CO₂ showed a much more complex behavior because of the equilibrium

Covergas -- heavy water -- ion exchanger

97% were always fixed in the resins, only 0.45% was found in the covergas and 2.6% in the heavy water. The maximum concentration on CO₂ in the covergas was found to 800 ppm by volume.

3.3 Secondary system

Only SiO_2 was measured routinely from the chemical group, all other controls of the demineralizer system were done by the operating staff.

In 1967 the fresh water quality changed. Studies had to be done for a new layout of the system.

4. Special events and observations

During the 20 years of reactor operation a number of special events occurred, which had some impacts on the reactor, or which at least were so curious that they caused long time discussions. Some of these events will be given in a short form in this chapter.

4.1 Defective fuel element in 1963

In 1963 the cladding of one metallic fuel element failed. The chemical reaction between the heavy water and the uranium released a large amount of the fuel into the water. The primary system got very strongly contaminated, all activity levels of the reactor were exceeded. All the contamination by fuel, found in the following years, were caused by this failure.

The highest concentration of uranium found in the water just after the failure was 0.01 ppm. The dose rate was especially high at the overflow tank. In crud samples from this tank 3.8 % uranium were found.

All crud samples collected since this time contained higher concentrations of uranium.

4.2 Biological shield cooling system

As mentioned in chapter 2.4 the first biological shield was a double walled steel tank. It was cooled by demineralized water in stainless steel coils, which were fixed by cast lead.

A leak occurred in november 1963.

Water flowed out from a hole , and this water contained a high concentration of NH_4Cl . This salt was used as a fluxing agent during the casting of the lead.

There was the risk that because of more corrosion the leak would get larger and larger, and that the reactor could have reached its end of life - only a few years after startup.

After long discussions it was decided to use glycol instead of water as a cooling fluid. This worked for some while , but only also from time to time, very effectively. Probably some kind of cement was formed from lead-oxyds with the glycol, sealing the leak. However sometimes also glycol was leaking from the tank. Furthermore the glycol underwent radiolytical decomposition. Among the many formed organic compounds (we spent a long time for the identification) were also some organic acids, and the risk for further corrosion increased.

Finally water was used again as the coolant, and the leaking water was circulated in a by-pass. Fortunately for the FR2 and all of us, the leak never increased and the cooling circuit as well as the reactor could operate until 1981.

4.3 Contamination by Ag-110m -----

Also soon after the reactor power increase, contamination of the primary system caused a serious problem for the operation. Obviously a silver plated component or a larger number of silver solder connections were in the core. (Because there was no cadmium in the water, control rods could be excluded).

While the concentration of Ag-110m in the coolant remained moderate, surfaces got heavily contaminated. On flow meters, brought to the laboratory for decontamination, 3 to 5 mCi Ag-110m were deposited. Chemically several mg silver were found on such flow meters. The specific activity was determined early 1967 to 4 Ci/g Ag. From such high specific activity it was evident, that the source was in the core.

The source could never be identified, but it exhausted during the years. Ag-110m contamination however was in the primary system until the final shutdown. In the purification resins, Ag-110m was always one of the strongest activity.

4.4 Contamination by W-187 -----

Because of a failure of a D₂O pump in the high pressure loop, a strong contamination of the primary system by W-187 (half life 24 hours) occurred.

The behavior of the tungsten was different if compared to the silver. The tungsten did not plate out on surfaces, it was removed within a short time by the purification system.

4.5 The " aceton effect"

The most curious und up to date not explainable effect was discovered in the early 70ties. Sometimes in the primary coolant the el.conductivity went up to 5 μ S/cm and the pD-value dropped below 4. This effect occured always if the reactor was shutdown.

After a long search it was discovered, that to operators cleaned some parts with aceton before inserting into the core. During this process some aceton leaked into the heavy water. Performed experiments showed, that as less as 30 grams of aceton, added to the bulk heavy water, caused this effect.

A pD -value of 3, as found after adding 50 g of aceton. In 23 tons of circulating heavy water, that means 23 mols of acid. The added aceton however was only 1 mol. Furthermore a radiolytic decomposition of the aceton could be excluded, because the final pD and conductivity values were attained only 20 minutes after adding the aceton, and the dose rate in the core was low because of shutdown.

The only explanation seems the release of anionic species from surfaces, caused by the aceton. The amount of such species will be limited, and in deed, more than 50 grams of aceton did not enhance the effect. However with the possiblities in the laboratory no anion could be identified. Because of the high tritium concentration of the D₂O it was not possible to give samples to an other laboratory.

The "aceton effect" was never a hazard for the reactor, because the purificatin system cleaned the heavy water quickly. The effect however remains a curiosity

4.6 SiO₂ -dust

In 1975 large amounts of white dust were blown into all rooms of the reactor area. The dust consisted nearly of pure SiO₂, with only a small concentration of CaO, it has been in a soft and easy to dissolve form.

The fresh air system was checked and found o.k. The source was finally found in the humidifiers of the fresh air. Here demineralized water was used from the make-up demineralizer of the secondary coolant system. By false operation the resin was inactive, and the SiO₂ concentrated in the water more and more, until nearly saturation conditions were attained. The highest concentration found in the make-up water was larger than 100 mg SiO₂/l (Fresh water contained only 15 mg/l SiO₂).

By replacing the resins, the problem was solved, but the dust has been found for a long time in electronic parts.

4.7 "Acid rain effect"

As described before the secondary system of the reactor FR2 was operated with demineralized water. Normally the electrical conductivity was around 10 µS/cm and the pH value at 6.0 . Depending on weather conditions, however the pH value dropped below 5.3 and the λ was raised to 40 µS/cm. The reason for this effect was found in the uptake of SO₂ from the air.

SO₂ concentrations in the air were especially high in the winter time. While the average values were in the range of

0.05 mg/m³, maximum values were found up to 0.4 mg/m³.
Per hour 3•10⁶ m³ of air passed through three towers, cooling
2000 m³/h of the water. The highest values of SO₄²⁻ found
in the water was 10.5 mg/l.

Balance calculations showed a good agreement between the
concentrations in the air and in the water, assuming 100%
efficiency for the 'washing out' of the air. Furthermore
it was found, as expected, that only a smaller fraction
of the SO₂ in the air was oxidized to SO₃, pointing
to a source not too far from KFK.

It should be mentioned that the described effect could only
be observed because the system was operated with demineralized
water. It can be compared with the 'acid rain' outdoors,
which caused so much trouble to the environment during the
last years.

4.8 Measurements at the stack -----

Normally no measurements were done from the chemical group
at the stack. Health physics people did here the investigations.

In 1971 Br-87 was detected in the exhaust air. A large cooling
machine was a defect and released FRIGEN to the atmosphere, just near
the inlet for the fresh air of the reactor. A fraction of this air
is cooling reactor channels and got activated. (By this usually
14 Ci of Ar-41 is formed per hour at 44 MW.). It was found, that
the FRIGEN contained some bromine, which got activated. Later on
also the expected Cl-38 was found. Because of its shorter half life
it was hidden behind the Ar-41.

In 1975 the isotopes I-123, 124, 125 and 126 were discovered
in the exhaust air. The source was a broken Xe-irradiation

capsule in the reactor core. These were so unusual nuclides for a reactor that the source was quickly found.

Since about 1972 Hg-197 and Hg-203 got released from the stack. The released activity was in the same range as the normal release of I-131 :

per week :	$7 \cdot 10^{-5}$	Ci I -131
	$3 \cdot 10^{-4}$	Ci Hg-197
	$3 \cdot 10^{-5}$	Ci Hg-203

The source could be localized in the reactor, but not identified and not removed.

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- 6 Schieferdecker, Bestimmung von Radionukliden in Biologischem Material, KFK-810 (1968)
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Table 1

Primary system of the FR2

Coolant	<ul style="list-style-type: none"> - Heavy water with an average concentration of 99.70 Mol% D₂O - total inventory 30 m³, circulating volume 23 m³ - flow rate 2000 m³/h - core outlet temperature at 12 MW 50 °C, at 44 MW 85 °C
Purification System	<ul style="list-style-type: none"> - 180 liters ion exchangers, consisting of a 1 : 1 mixture of the strong acidic and strong alkalic resins S100 and M500 (LEWATIT) (H⁺ resp. OH⁻ - form) - bypass operation with 2.5 m³/h - resins were not requalified after use
Surfaces in Contact with the D2O	<ul style="list-style-type: none"> - 2.3 m² AlMg3, in the core - 103 m² Al-99.5, primary vessel, partly in the core (until 1966 with the cladding of the metallic fuel elements about 150 m²) - 231 m² zircaloy, the cladding of the oxidic fuel elements in the core - 800 m² stainless steel 1.4571 (18% Cr, 10% Ni, 2% Mo), all outside of the core; from this about 660 m² were in the heat exchanger

Table 2

Chemical measurements for the reactor

Primary system	- D ₂ O concentration	r
	- concentration of metallic and nonmetallic impurities	r
	- determination of alpha, beta and gamma radioactivity	r
	- uranium concentration (until 1972)	u.r. (r)
Covergas	- radioactive nuclides	r
	- nonradioactive impurities	u.r.
	- deuterium	u.r.
Secondary system	- SiO ₂	r
	- other impurities	u.r.
Measurements for experiments	- Steam cooled loop : inactive and radioactive substances	r
	- Pressurized water loop : as before, especially Cl and oxygen	r
	- Pressurized helium loop: tritium and impurities	u.r.
	- Low temperature systems: impurities	u.r.
Other measurements	- activity measurements at the exhaust air at the stack	u.r.
	- investigation of radiation stability of structural materials esp. plastics, glasses etc., as well as of samples for irradiation	u.r./f.
	- metallographic investigations of contaminated materials	u.r.
	- corrosion tests	u.r.
	- decontamination of reactor components and materials	u.r./f.
r. = routinely, at least weekly u.r. = upon request f. = frequently, but not with a fixed time scale		

Table 3

Analysis of the heavy water*

electrical conductivity	0.6 $\mu\text{S}/\text{cm}$ 0.1 $\mu\text{S}/\text{cm}$ behind purification
pD	6.8
Al	0.01 ppm
Fe	0.05 ppm
Cr	0.03 ppm
Ni	0.02 ppm
U	lt. $5 \cdot 10^{-4}$ ppm
Cl^-	0.025 ppm
Na^+	0.02 ppm
D_2O_2	1 to 10 ppm
D_2	0.3 mg/l
CO_2	240 ppm
other gases	depending on covergas impurities
crud level (particulates)	lt. 10 ppm

*average values from 1966 to 1981

Table 4

Radionuclides in the heavy water

Nuclid	Half live *	activity** Bq/g
Alpha activity		4 to 20 •10 ⁻⁵
H-3	12.3 a	2.4 •10 ⁸ (final value)
C-14	5730 a	2 to 8
N-16	7.1 s	30,000
O-19	29.1 s	9,000
F-17	64.8 s	16,000
F-18	119.7 m	3,000
Mn-56	2.58 h	100
Cr-51	27.7 d	75
Co-60	5.27 a	0.75
Zr-95	64 d	2.3
Tc-99m	6.0 h	240
Mo-99	66. h	n.d.
Re-188	17.0 h	2500
Ag-110m	250 d	0.7
Na-24	15.4 h	150
Sr-92	2.7 h	40
Tc-101	14.2 m	180
Tc-104	18.2 m	90
I-131	8.0 d	3
I-134	52.0 m	50
Cs-138	32.2 m	100
Np-239	2.3 d	75

* Values taken from W.Seelmann-Eggebert, Chart of Nuclides (1981), published by Kernforschungszentrum Karlsruhe.

** Average data for 1980/1981 without defective fuel pins.

Table 5

Surface contamination of the primary system

Nuclide	Bq/cm ²
Zr-95	2800
Cr-51	9000
Co-60	370
Ag-110m	3700
Alpha	0.006 to 0.06
Uranium	g/cm ² : 10 ⁻⁷

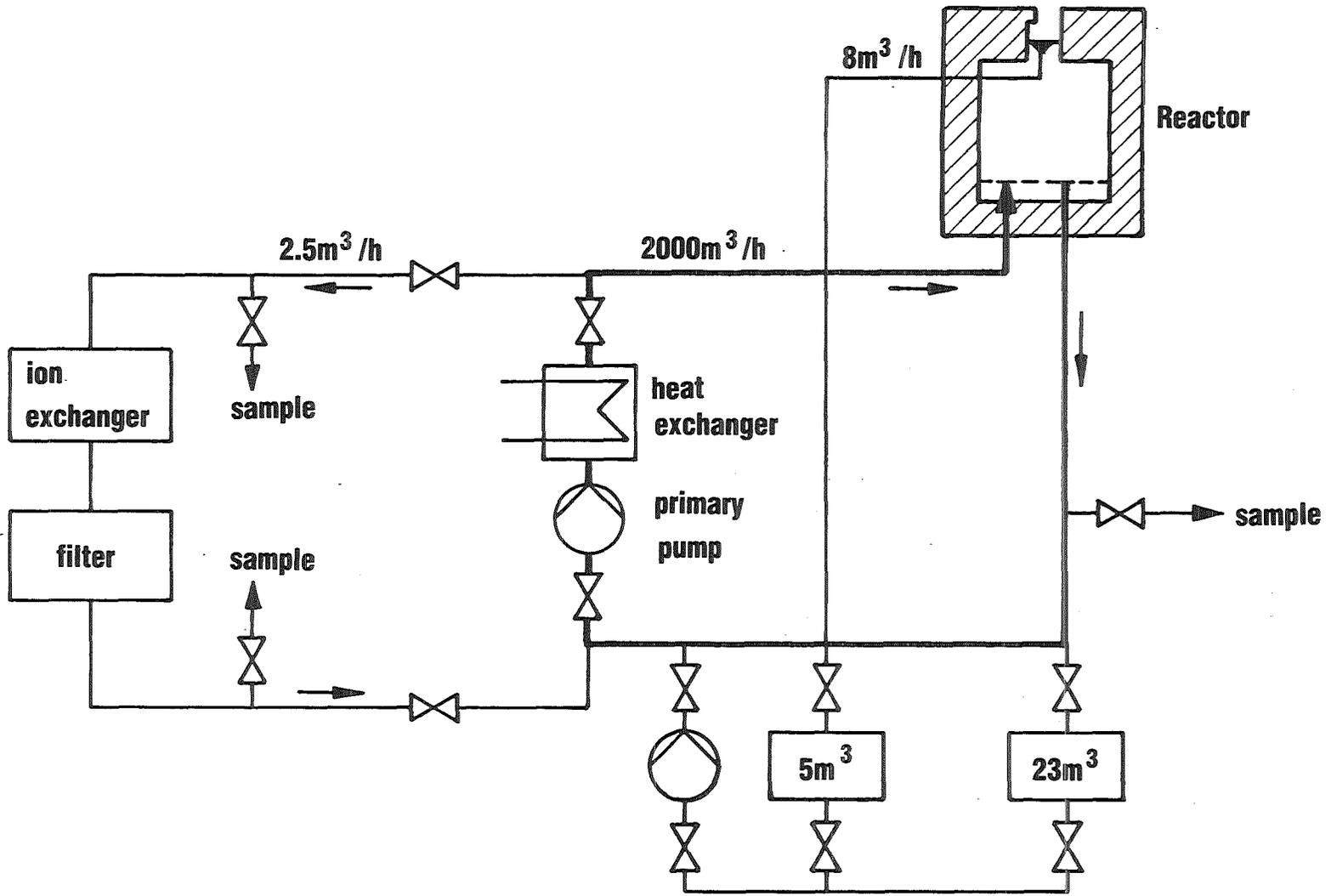


Fig.1: Primary System of the Reactor FR2

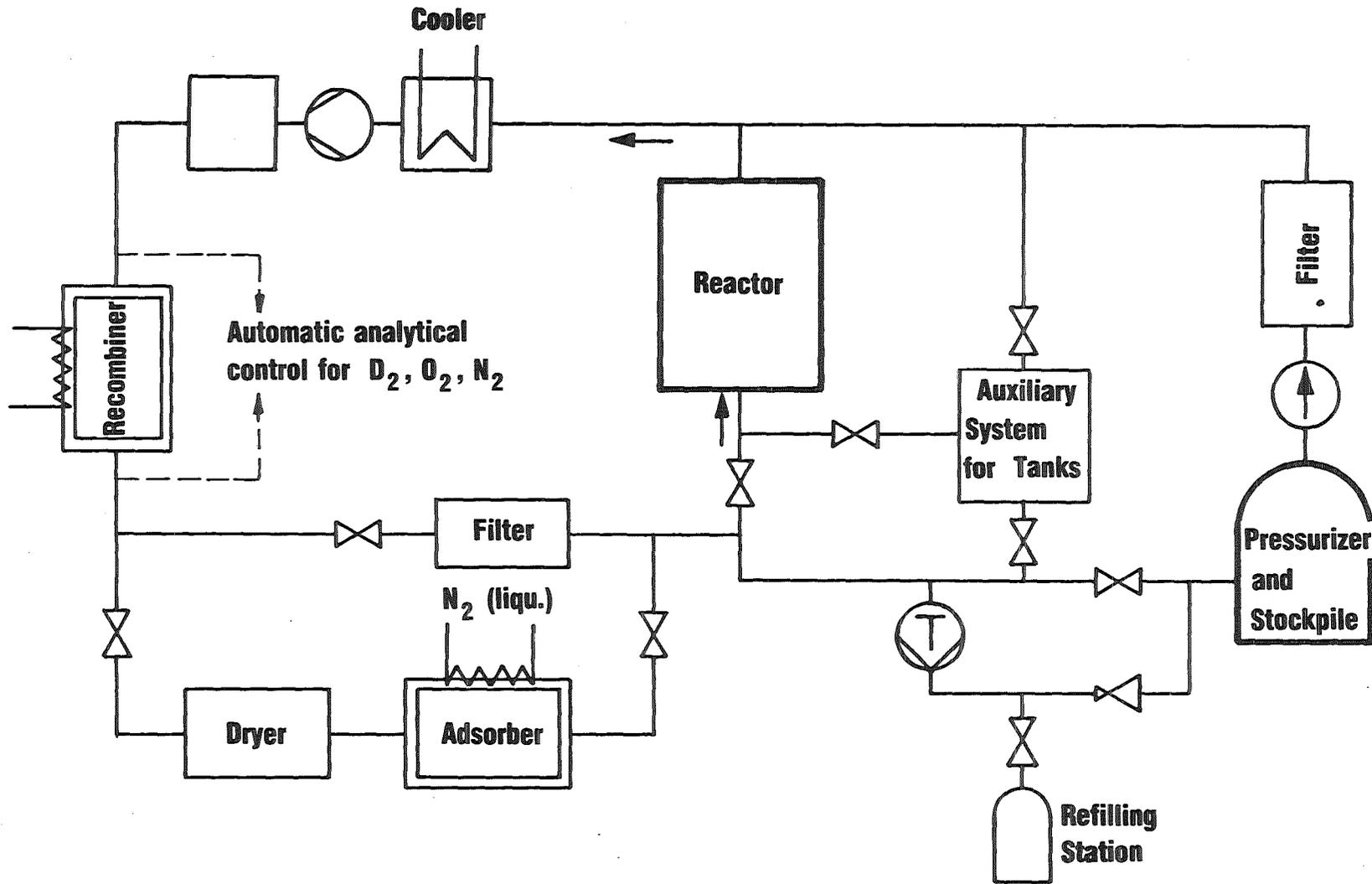


Fig.2: Covergas System of the Reactor FR2

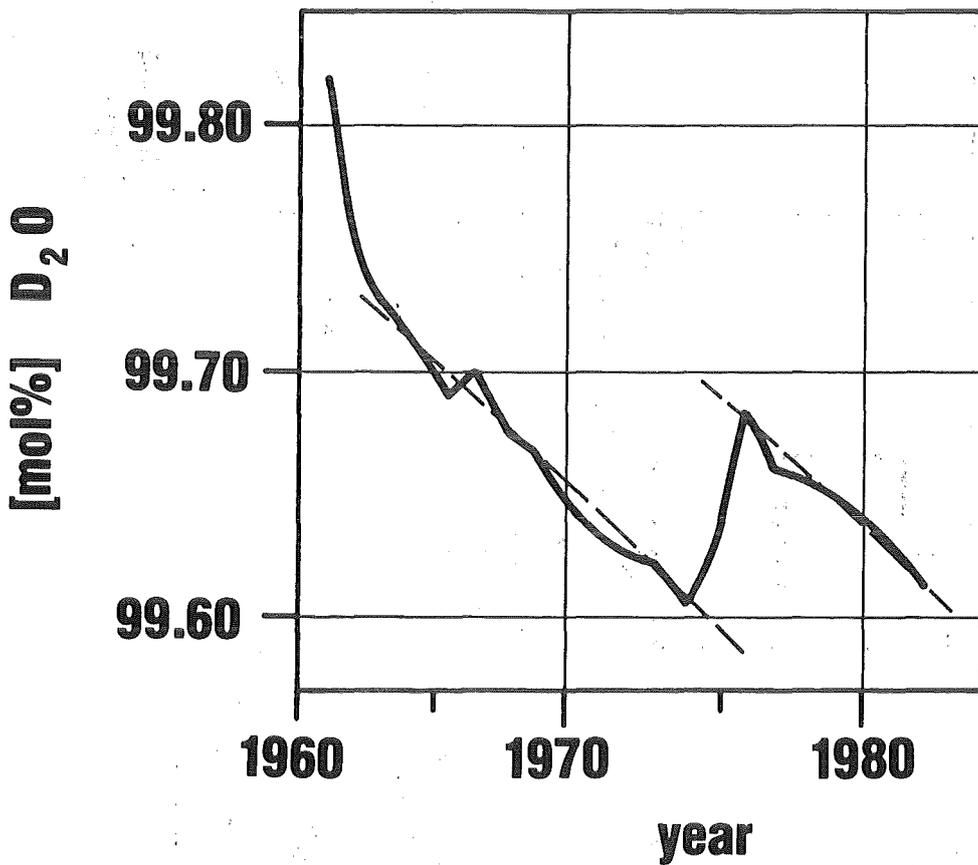


Fig.3: Isotopic Concentration of the Heavy Water

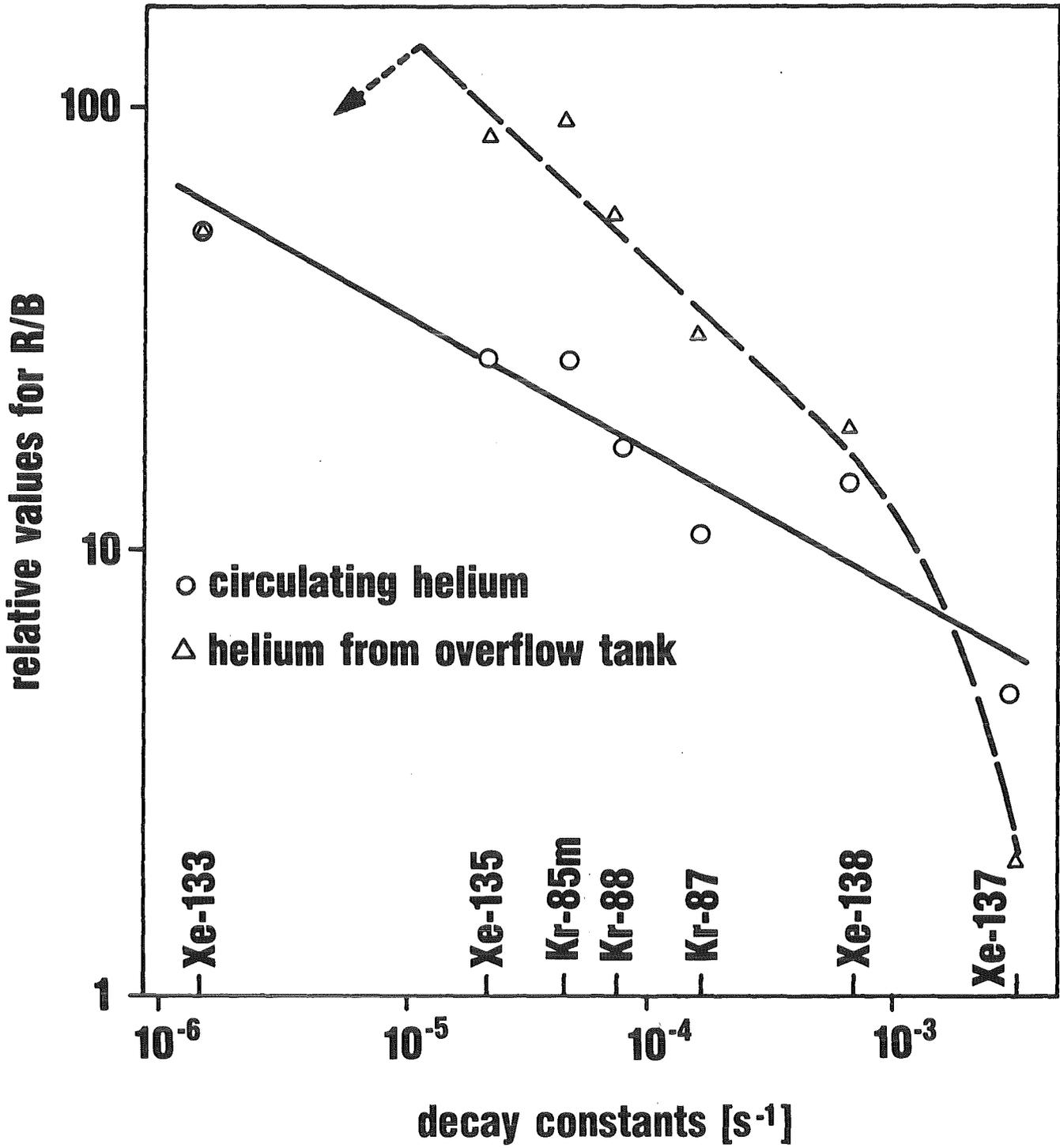


Fig.4: Fission Gas Release to the Covergas.
Shown are relative release to birth ratios
vs.the decay constants of the gases.